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ANALYSIS OF GAS CONSTITUENTS FROM SEALED CONTAINERS OF PLUTONIUM OXIDE MATERIALS

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ABSTRACT

The safe storage of pure and impure plutonium oxide materials in sealed containers is a current Department of Energy (DOE) concern. Plutonium oxides sorb moisture from the atmosphere, and the subsequent radiolytic and/or chemical decomposition of the water has been thought to generate excessive hydrogen pressures inside sealed containers. Eleven sealed containers with ten grams each of plutonium oxide materials have been studied for up to four years. The sealed materials were representative materials from the DOE complex and contain less than 0.5 weight percent water. The samples were kept close to 23^0 C. We report the final gas analysis of the headspace gas of these containers using gas chromatography, mass spectrometry and Raman spectroscopy. The results show that none of the containers have pressurized significantly, and that hydrogen was not generated in significant quantities.

INTRODUCTION

Until the late 1980s, a primary mission of the Department of Energy (DOE) has been the production of nuclear materials for nuclear weapons. Termination of the Cold War in 1989 and the subsequent nuclear weapons treaties dramatically decreased the plutonium material inventory needs in support of nuclear weapons. These activities resulted in the consolidation of nuclear material inventories and activities, generating substantial amounts of surplus nuclear materials ranging from plutonium metal and pure oxides to impure plutonium residues. Packaging and storage of these materials in physically and environmentally safe configurations for significant time periods were required.

In 1993 the Defense Nuclear Facility Safety Board (DNFSB) and the DOE Office of Nuclear Safety examined the storage of metal and oxides at the Rocky Flats Plant, which ultimately resulted in recommendation 94-1, calling for a standard to define the processing and storage of plutonium bearing materials. This recommendation generated a standard for storage of plutonium metals and oxides, DOE-STD-3013-2000, which is now in its fourth revision.[1] The current DOE 3013 Standard is limited to metal and oxides, which contain greater than 30 weight percent plutonium and uranium. The 3013 Standard requires that the oxide be calcined to 950^0C for two hours in an oxidizing environment. Before packaging, the oxide is required to have less than 0.5-weight percent moisture. Up to five kilograms of the stabilized oxide material is subsequently sealed in a set of two nested and welded stainless steel containers. The material within the container must have a power less than 19 Watts.

The processing, handling, and storage of plutonium metal has been understood for many years based on results from plutonium manufacturing and storage of components. However, the long-term storage of pure and impure plutonium oxides in hermetically sealed containers is not well understood and presents some unique challenges in storage. Of current concern is the pressurization of the sealed containers loaded with actinide oxides, where several causes of pressurization have been identified. Chemical and radiolytic reactions can generate gases in the containers from material decomposition and the reactions and rates of reactions are areas of ongoing research. Plutonium oxides strongly adsorb gaseous species such as water and the subsequent decomposition of the adsorbed species can lead to pressurization of a sealed container.[2,3] Contact of plutonium oxides with organic materials will also result

in gas generation. Chloride salts that can adsorb water are frequently present in oxide residues. In addition there is a potential for the production of Cl_2 or HCl from these salts resulting in subsequent container corrosion.[3]

Vaporization of adsorbed species due to a temperature increase inside the container may lead to a nominal pressurization. Water vaporization, for example, could contribute up to ~300 psi to container pressurization, and is limited by the equilibrium between the adsorbed water and vapor phases.[4,5] Additionally, a container with a hydrogen and oxygen atmosphere could experience a deflagration or a detonation, depending upon the conditions within the container. From past experience, these pressure pulses are not considered a concern for containers packaged to the 3013 Standard criteria because it is believed that the atmosphere will not reach combustible limits. The current 3013 Standard includes a conservative equation for derivation of a bounding pressure increase based on complete decomposition of water to generate hydrogen. From this equation, pressurization up to 700 psi can be derived. The equation is conservative and considers only factors that contribute to gas generation and not those factors that may lead to recombination.

Efforts are underway in the 94-1 Program to determine reaction rates and bounding conditions of gas generation and corrosion in sealed containers of oxide material. The present investigation begins to define the long- term gas generation behavior of plutonium oxide materials in hermetically sealed containers. Ten-gram quantities of plutonium oxide residues with a range of impurities were sealed and monitored for pressure, temperature, and gas constituents. The experiments were terminated after approximately four years in surveillance and a final gas analysis was obtained. The information is significant to both gas generation modeling and long-term surveillance programs for storage.

EXPERIMENTAL

Methods and Equipment. Figure 1 shows a typical container used here to study gas generation in ten-gram samples. Each container is manufactured from 304 stainless steel and is equipped with two type K thermocouples, a Stellar strain gauge pressure transducer, a particle filter, and a low-volume sampling system. The gas sampling system is made from a short high-pressure nipple and two high-pressure valves. The internal volume of the gas sample is between 0.3 and 0.4 cm^3. One of the thermocouples is positioned to measure oxide temperature and the other thermocouple is positioned to measure gas-phase temperature. Not shown in Figure 1 is a bailed bucket that holds the oxide material. The bailed bucket is fabricated from 316 stainless steel. The free volume of the reactor ranges from 35 to 53 cm^3 without oxide. The pressure transducers connected to Omega Engineering DP-80 strain gauge readouts. The containers are at ambient temperature during the experiment.

Figure 1. Photograph of 10-gram storage container equipment.

Each container is leak-checked after assembly in the form shown in Figure 1 before addition of the oxide. The first leak-check is a rate-of-rise vacuum leak-check. The container is then subjected to a 16-hour pressure leak-test by pressurizing the container between 70 and 75 psia. All leaks are corrected before proceeding. Before loading the container with oxide, the container is disassembled and the bailed container removed and placed in the plutonium glove box line. Ten grams of oxide is weighed to the nearest milligram and subsequently loaded into the storage

container in an open front hood. The container is sealed, evacuated, and vacuum leak check is performed. If the container is leak-tight the selected storage gas is added (He, air or N_2) and the initial gas pressures and temperature recorded. The container is then placed in its permanent storage location and connected to the data acquisition system for pressure and temperature monitoring.

Periodically each container is removed from storage and an interim headspace gas sample is obtained and characterized by a residual gas analysis mass spectrometer. A gas sample is isolated from the container between the two high-pressure valves, and then expanded into the mass spectrometer introduction port where an expanded pressure is measured. After pressure measurement, the gas is expanded into the expansion chamber to lower the gas pressure to approximately 0.15 torr. The gas is then introduced into the mass spectrometer and a mass spectrum recorded. At least 2 spectra are acquired, saved and analyzed for each sample.

A final gas analysis was conducted using a series of analytical methods to obtain confirmation of the gas constituents. The sealed container was transferred into the glove box line and connected to a gas manifold that allows for characterization for pressure by volume expansion and gas composition by Raman spectroscopy, gas chromatography, and mass spectrometry. This approach allows for confirmatory identification of gas species, which may have overlapping peaks or interference in mass spectrometry. A gas sample is obtained by initially expanding a portion of the headspace gas into a Raman chamber for measurement. The gas is then expanded into the gas manifold. This gas is then sampled by a HP 5890 gas chromatograph and an Omnistar RGA. For each container, the gas expansion is repeated up to three times until the complete headspace gas has been expanded into the manifold. Pressure and temperature measurements are recorded during the gas expansion steps, which allow the initial container pressure to be determined. It is noted that in some cases during the surveillance period, several pressure transducer and /or readouts directly on the container became questionable. The pressure readings became insensitive to temperature and displayed data that did not agree with pressures obtained during gas expansion. In some cases, pressure readings jumped in step functions and were not reasonably consistent. In these cases, the gas expansion method was used to determine the final container pressure.

When conducting the final gas analysis on the containers, Raman spectra were not obtained on five samples: PPSL-365 as received, ARF-102-85-295 as received / 950^0C calcination, ARF-102-85-223 as received, and 5501407 as received. An unidentified peak in the gas chromatograph of these containers resulted in addition of the Raman capability for identification of the unknown gas species.

Oxide Material. Plutonium oxide items were obtained from various Hanford and Rocky Flats Environmental Site (RFETS) processes and include samples from BLO39-11-14-004, PPSL-365, ARF-102-85-223, ARF-102-85-295, 5501407, and RF669194. The material description from the Hanford items include: item PPSL-365 was processed in a prototype model of Hanford's vertical calciner; item BLO-39-11-14-004 contains fuel-grade plutonium with appreciable americium; and ARF-102-85-223 and ARF-102-85-295 were RFETS items sent to Hanford and stored. The material description from the RFETS items include: item 5501407 contains a mixed plutonium/uranium oxide prepared from a hydride oxidation process, and item RF669194 contains a residue from a plutonium / uranium oxide process. The oxides materials were previously characterized by the 94-1 R&D Program.[2] Ten-gram samples for the surveillance containers were taken from material as-received at LANL, and following stabilization at 600^0C and 950^0C calcination.

RESULTS

The characteristics of the oxide material that were sealed in the 10 gram surveillance containers are listed in Table 1. A range of material types was prepared under a range of conditions and sealed for several years. Table 1 includes the major impurities. A complete chemical analysis was done previously.[2] The plutonium / uranium content ranged from 85 percent oxide to a fairly impure item with approximately 20 weight percent salts (as received ARF-102-85-295). Item BLO39-11-14-004 is characterized as a pure fuels-grade oxide and contains americium, with higher heat generation. The stabilization parameters varied from calcination at 950^0C and 600^0C, to material that was stabilized years earlier at Hanford or RFETS under various conditions (as received). The gas atmosphere in the sealed containers also varied from helium, air or nitrogen.

The moisture content was determined by supercritical fluid extraction (SFE) and interstitial gas analysis (IGA). Results from SFE measurements are considered a lower limit and are consistently lower than the IGA values except

for one sample. It is felt that SFE sample storage methods may dry the samples prior to the SFE measurement. These samples were packaged in SFE containers, stored in sample jars with Drierite™, which can potentially remove moisture from the oxide depending on which material has the higher heat of adsorption for water.

Table 1. Summary of material characteristics [2] and storage conditions examined in this study. Properties not determined are labeled nd.

Item	Calcination T, °C	Pu/U wt%	Cl wt%	Other Impurities, wt%	H_2O, wt% SFE[a]	IGA	Container Volume, cc	Sample mass, g	SSA, m^2/g	Fill Gas	Storage Days
BLO39-11-14-004	As received	85	<0.5	6 - Am 0.2 - C	0.6	nd	36.8	10.0	nd	Air	1526
PPSL-365	As received	83	<0.5	1.5 – Fe	<0.1	<0.1	37.5	10.0	2.3	He	1679
	600	nd	<0.5	nd	<0.1	nd	39.2	10.0	2.2	He	1605
	950	nd	<0.5	0.8 - Fe	<0.1	nd	37.3	10.0	0.7	He	1598
RF669194	As received	15/69	<0.5	0.5 – Fe 0.3 – Be	<0.1	0.3	53.4	10.0	3.0	He	861
5501407	As received	63/11	<0.5	4.3 – Ni 4 - S	0.4	1.2	57.5	10.0	4.9	N_2	1128
	950		<0.5	2 - Ni	0.2	<0.1	56.7	10.0	0.5	N_2	920
ARF-102-85-223	As received	66	11.2	6.6 - K 4.8 – Na 0.9 - Mg	0.1	1.2	57.3	10.0	3.5	Air	1331
	950	nd	5.5	1.9 - K 1.5 – Na 0.5 - Mg	<0.1	<0.1	53.5	10.0	0.5	Air	960
ARF-102-85-295 chunk	As received	31	20	6.8 – Mg 5.4 – K 3.7 - Na 2 – Ni 2.5 - Fe	<0.1	nd	37.2	10.0	(chunk)	Air	1652
	950	43	7.7	5.4 – Fe 4.1 – Ni 4.0 – Mg 2.4 - Na 2.3 – K 1.3 - Cr	0.2	nd	63.2	10.3	(chunk)	Air	1331

a) SFE values are considered a minimum moisture content value.

The storage conditions for this study varied as listed in Table 1. Air, helium or nitrogen was used as the storage gas in the containers, which were based on requests from the packaging sites. The volume of the empty sample containers varied from 37 – 63 cm^3. These containers were stored under ambient conditions. The temperature of the small samples fluctuated by a few degrees around 23^0C depending on the daily glove box temperatures. BLO39-11-14-004 was typically one degree warmer than the other ten samples.

The results of the final gas analysis are shown in Table 2. Table 2 presents all of the gas phase species observed by Raman spectroscopy and by gas chromatography (GC). Gas constituent identification is verified in the mass specta; however, concentrations are not calculated from the mass spectra due to the difficulty of quantifying the instrument response. Sensitivity between 0.1 and 1 Torr for all of the gas-phase species is achieved by both the Raman and GC instrumentation, except Raman does not detect the monatomic gases. The error in the final pressure measurement was ±10% (2σ) due to uncertainties in the volumes of the containers. Thus, only the four ARF-102-85-xxx containers that were packaged in air had pressure changes outside of the estimated error. In each case the pressure decrease is due to oxygen depletion. The Raman results and the GC results are independent of each other. Nevertheless, the two methods agreed either within 5% or a few Torr in most cases. In two cases the difference

between the two methods for the nitrogen pressure was about 20%. The results presented in Table 2 and in the graphs are the GC results.

The final gas analysis for the major constituents fits well with the original observations. However, the original observation of hydrogen exceeding a few Torr is not observed in the final analysis. The original observations are from mass spectral data, which is difficult to quantify for hydrogen. The trends of all of the species observed in the final analysis for the containers that did not leak are given in Figures 1-3. Data for sample 5501407 calcined at 950^0C is only available for the final gas analysis, therefore the data trends are not plotted.

Table 2. Summary of gas constituents determined in the final gas sampling of the oxide containers.

Item	Calcination T, ^{o}C	Fill Gas	$P_{initial}$ Torr	P_{final} Torr	ΔP, Torr	Suspect Leak	He Torr	N_2 Torr	O_2 Torr	CO_2 Torr	N_2O Torr	H_2 Torr	CO Torr
BLO39-11-14-004	As received	Air	611.7	615	3	Y[1]	0.0	491.4	111.7	8.2	3.5	0.4	0.0
PPSL-365	As received	He	759.7	722	-38	slight[2]	710.5	11.6	0.0	0.0	0.0	0.0	0.0
	600	He	614.0	589	-25	N	589.1	0.0	0.0	0.0	0.0	0.0	0.0
	950	He	577.8	524	-54	Y[2]	226.6	276.9	0.0	19.9	0.0	0.8	0.0
RF669194	As received	He	nr	598		slight[2]	585.4	3.0	0.0	6.3	1.9	0	1.5
5501407	As received	N_2	551.3	582	31	N	0.0	564.0	0.0	9.7	8.8	0	0.0
	950	N_2	nr	601		N	0.0	592.2	0.0	5.1	3.7	0	0.0
ARF-102-85-223	As received	Air	573.0	480	-93	N	12.3	428.5	17.6	14.2	5.8	2.2	0.0
	950	Air	586.4	523	-63	N	8.4	437.4	56.4	13.7	6.3	0.9	0.0
ARF-102-85-295 chunk	As received	Air	592.6	462	-131	N	2.0	392.3	43.4	20.0	3.4	0.8	0.0
	950	Air	539.0	482	-157	N	0.0	408.4	29.1	30.5	12.3	1.7	0.0
Blank		empty		0.6		N	0.0	0.3	0.0	0.0	0.0	0.3	0.0

1. Intermittent gas sampling indicated a total pressure decrease and an oxygen concentration decrease. A leak that developed in the container, or in the gas sampling manifold is suspected because the final analysis and the intermittent analysis are not consistent.
2. A leak is suspected due to the presence of air constituents in the container filled with helium.

DISCUSSION

A variety of oxide residues have been stored for multiple years in sealed containers. The samples conservatively contain less than one weight percent moisture and at best a range of water content can be provided based on the moisture measurement data and sample handling. The data in Table 2 show that no pressure increases are observed in these ten-gram samples stored at room temperature conditions. In the leak free samples that contain air, a pressure decrease is detected.

Trends in the gas constituents are observed over time in Figures 2-4. In all cases, the detected increase in any gas component is less than five percent of the total gas. For those materials packaged in an inert atmosphere (He or N_2), see Figure 2, very little change is observed in the gas composition over time. There is a small increase in N_2O in 5501407 as received, which is attributed to the radiolysis of nitrogen with an oxygen source present. The oxygen source in this case may be due to small air leak in the container, or moisture on the sample.

For those materials packaged in an oxygen containing atmosphere, Figures 3-4, the oxygen is depleted, and after several years of storage and less than 10 percent is left in several samples. Additionally, both CO_2 and N_2O gases

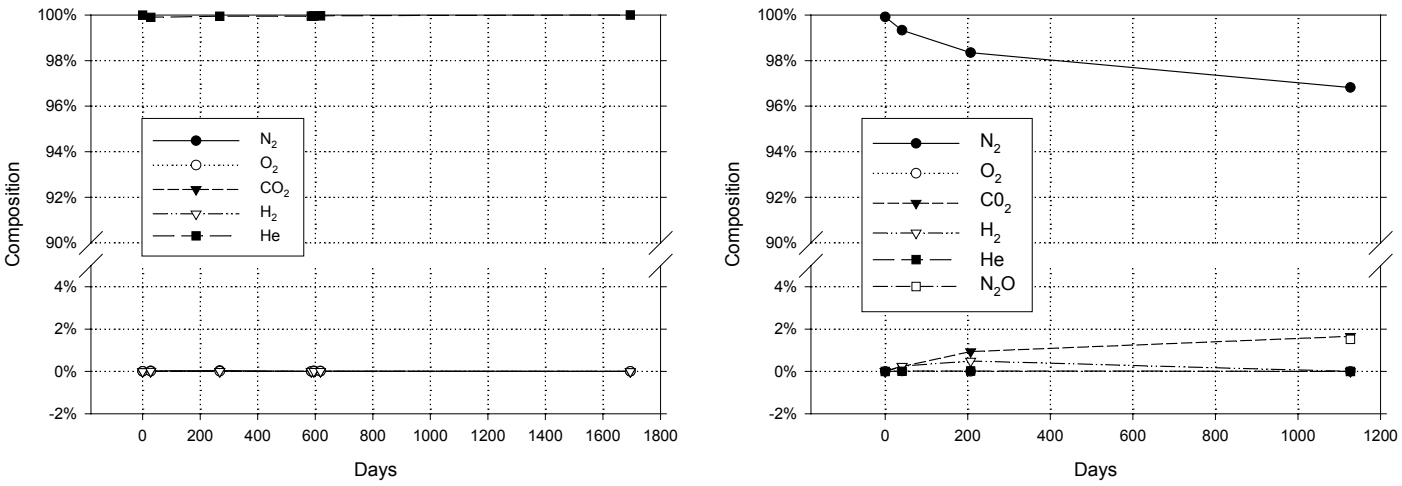

Figure 2. Relative gas composition as a function of time for PPSL-365 calcined at 600^0C (left) packaged in helium, and 5501407 as received (right) packaged in nitrogen.

are observed to appear in levels up to five percent. These trends are also observed in BLO39-11-14-004 during the early mass spectroscopy gas analysis, which indicate that O_2 (and pressure) is depleted in 178 days with less than two percent of O_2 left in the headspace gas. During the final gas analysis, a large leak was observed in the container, thus the data is not shown in a figure. Calcination has very little effect on the changes of the gas composition as a function of time, Figures 3-4. In ARF-102-85-223, calcination appears to result in a slower consumption of oxygen and slightly lower gas-phase CO_2 and N_2O concentrations. The amount of oxygen in the gas-phase generated in CO_2 and N_2O does not equal the amount of oxygen depleted. Additionally, the amount of CO_2 observed in the gas-phase does not represent all of the CO_2 produced. Most of the CO_2 may be bound to the surface of the oxide particles and does not show up in the gas-phase at room temperature. Heating the material to above 120 °C results in the material outgassing CO_2.[7] The same mechanism may occur for N_2O. Thus, the sink for all of the oxygen in these materials may be CO_2 and N_2O.

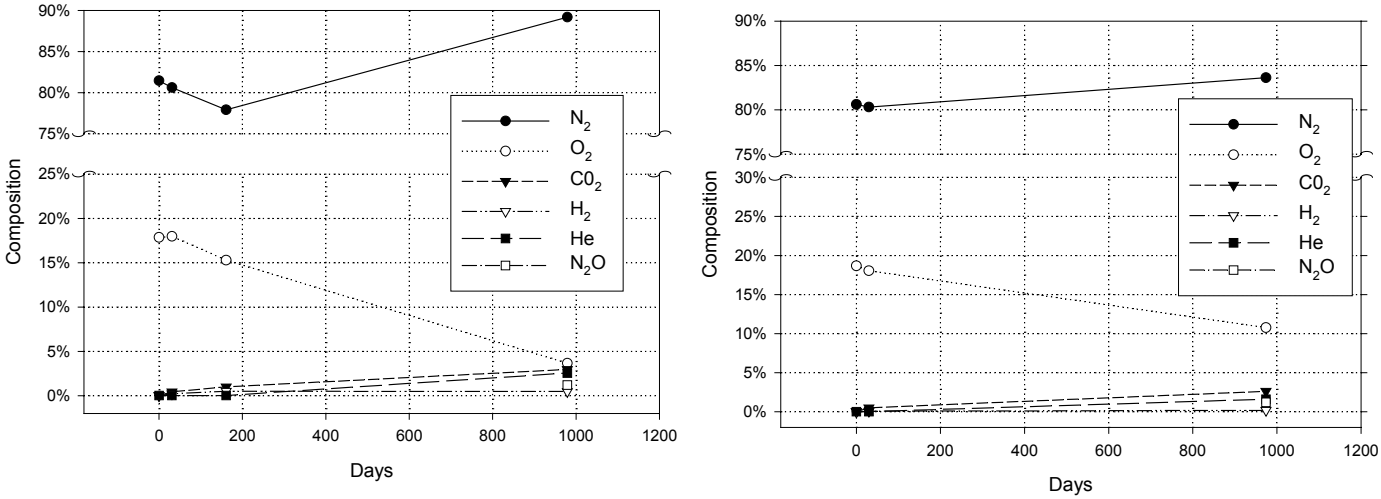

Figure 3. Relative gas composition as a function of time for ARF-102-85-223 as received (left) and calcined at 900^0C (right), both samples packaged in air.

Finally, and most significantly, very little H_2 is generated in these samples over time. In fact, most samples show that H_2 is detected at levels comparable to the experimental blank, where H_2 production may be attributed to

diffusion from the stainless steel. There is no correlation with the amount of H_2 generated and the amount of detected moisture on the material or the amount of plutonium. Additionally, from the Raman measurements, no water is seen in the gas phase. Any water that may be present is bound to the oxide surface.

These results observed here suggest that a variety plutonium oxide materials with low moisture levels as determined by SFE or IGA and no additional hydrogenous source will not generate hydrogen gas. This condition can be obtained by calcination to drive off reactive materials such as water and organics, and subsequently handling the material properly to minimize moisture re-adsorption. It is also observed that oxygen is depleted in the samples that have an oxygen source such as air, and that none of the samples indicate oxygen generation or the generation flammable gas mixtures.

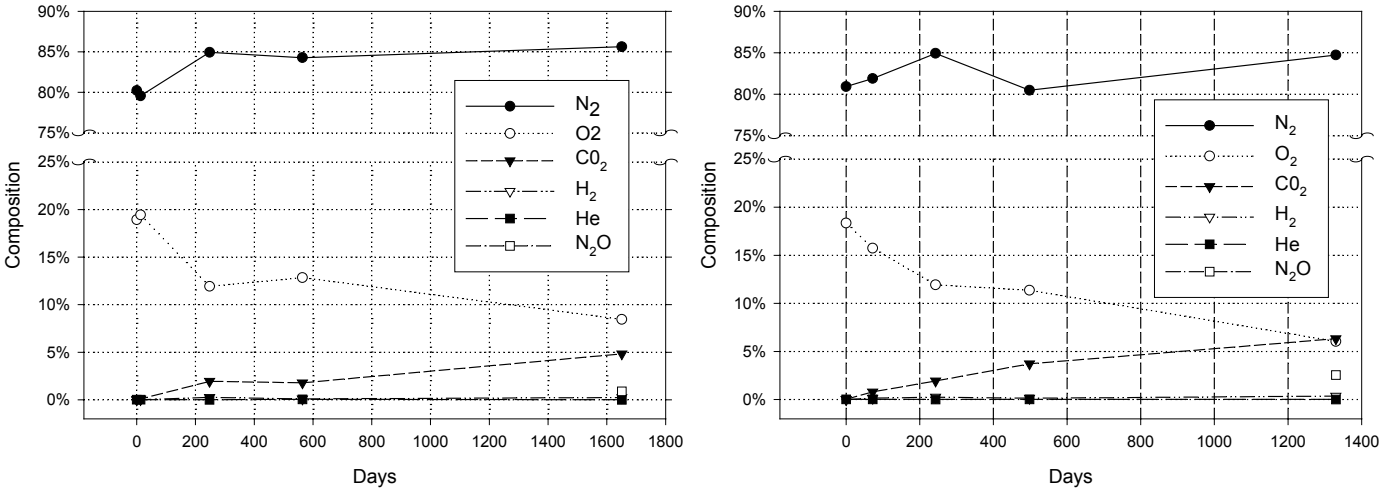

Figure 4. Relative gas composition as a function of time for ARF-102-85-295 as received (left) and calcined at 900^0C (right), both samples packaged in air.

ACKNOWLEDGEMENT
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